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ELECTROLYSIS OF SOLID POTASSIUM FERROCYANIDE UNDER PRESSURE

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Introduction

It is well known^{1,2)} that potassium ferricyanide is produced industrially from potassium ferrocyanide in aqueous solution by electrolytic oxidation. The experiments have not been carried out yet on the electrolysis of ionic crystalline powder under pressure at room temperature. In this experiment, the relations between the amount of electrolytic product at the anode and pressures are determined up to the pressure of 10,152 kg/cm² at room temperature using the powder of potassium ferrocyanide and some other electrolytic conditions are examined.

Experimentals

(1) Samples

(i) Potassium ferrocyanide trihydrate

It is recrystallized from aqueous solution of potassium ferrocyanide made by Merk and is used as 250 mesh fine powder. This sample is allowed to remain in the desiccator with saturated solution of $\text{NH}_4\text{Cl} \cdot \text{KNO}_3$ in order to be kept the stable state³⁾.

(ii) Potassium ferrocyanide anhydride

It is dehydrated by heating the recrystallized potassium ferrocyanide trihydrate at 110°C.

(2) Apparatus and operations

The high pressure apparatus and electrodes used for this experiment have been reported⁴⁾. The electrodes are made with 13 Cr-steel and the diameter of electrode surface is 8 mm. To determine the quantity of electricity an electrolytic gas coulometer is used and checked with a silver coulometer.

As for the experimental operations, the solid sample is compressed to a definite pressure and then electrolysed with the current density 0.0016 ~ 0.0032 amp./cm² until 5.74 coulombs passed through the sample. After that, releasing the pressure, the sample is analysed.

(3) Analytical method

An oxidation product at the anode, which is potassium ferricyanide, is found qualitatively by benzidine. Then, the amount of the oxidation product at the anode is determined by the iodometric method⁵⁾ as in this electrolysis of aqueous solution.

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2) G. Grube, *Z. Elektrochem.*, **20**, 334 (1914)

3) *Gmelins Handb. der anorg. Chem.*, **59**, 954

4) T. Yanagimoto, *This Journal*, **23**, 30 (1953)

5) F. P. Tradwell and W. T. Hall, *Analytical chemistry*, 640 (1935)

Results

(1) Potassium ferrocyanide trihydrate

The anode side of the sample electrolysed under pressure becomes reddish brown and the cathode side more white than the starting sample.

The relation between the pressure and the amount of the oxidation product for a definite quantity of electricity, 5.74 coulombs, is shown in Fig. 1. The oxidation product increases with the pressure, and above the pressure of 4,089 kg./cm² it reaches a constant value.

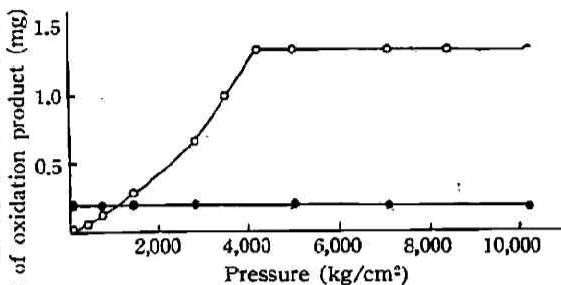


Fig. 1

○ Hydrate, ● Anhydride,
Quantity of electricity: 5.74 coulombs

In the case of atmospheric pressure the same experiment is carried out using the single crystal in place of the powder, but the oxidation product is a trace.

Next, this electrolysis under pressure is examined by changing the electrolytic conditions or the process of the pressure applied.

(i) Electrolytic conditions

a) At a definite pressure (1,410, 2,820, 4,935 kg/cm²) the sample is electrolysed with the current density 0.0016 amp./cm² or with 0.0032 amp./cm², but the yield does not change for 5.74 coulombs.

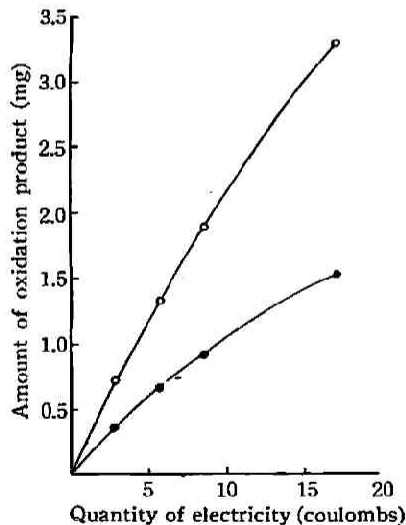


Fig. 2

○ 4,935 kg/cm², ● 2,820 kg/cm²

b) At a definite pressure the effect of the quantity of electricity on the yield is shown in Fig. 2. Increasing the quantity of electricity the current efficiency decreases, at higher pressure the decrement is smaller in value.

c) To research for the effect of electrode materials, the 13Cr-steel anode is covered with the Pd plate and the electrolysis is carried out under the pressure of 4,935 kg/cm², but the yield is the same as in the case of 13Cr-steel anode for 5.74 coulombs.

(ii) Process of the pressure applied

a) In either case of applying hydraulic pressure of 4,935 kg/cm² to the sample gradually or suddenly, the electrolytic product does not change.

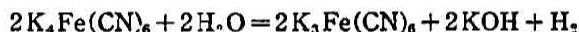
b) After the pressure of 4,935 kg/cm² is applied to the sample and is released until 2,820 kg/cm², at that pressure the electrolysis is performed. Consequently, the yield is the same as that of the sample directly compressed up to 2,820 kg/cm².

(2) Potassium ferrocyanide anhydride

The relation between the pressure and the amount of the oxidation product for a definite 5.74 coulombs is shown in Fig. 1, and the pressure effect is not observed.

Considerations

It is considered⁴⁾⁵⁾ under high pressure that the mobility of ions of ionic crystal decreases in the electric field. But, in this experiment the amount of the oxidation product on the trihydrate increases with the pressure as shown in Fig. 1. On the other hand, the pressure effect on the anhydride is not observed. Therefore, it is considered that the pressure effect is due to the existence of the water of crystallization. It was reported⁶⁾ that when the hydrous crystals, such as gypsum or cupric sulphate pentahydrate, were compressed at room temperature, the water of crystallization becomes unstable, depending on the magnitude of pressure by the shearing stress among the crystal grains. Also in the case of potassium ferrocyanide trihydrate, it is probable that the water of crystallization becomes unstable by the compression. Moreover, from the experiments of the process of the pressure applied it is known that the pressure effect is related to the magnitude of the pressure used in the electrolysis and not related to the compressing process as already mentioned. In aqueous solution potassium ferricyanide is produced by electrolytic oxidation as shown in the following equation¹⁾²⁾.



It seems that in the case of electrolysis of the solid trihydrate under pressure the part of water in the equation is performed by the water of crystallization which becomes unstable depending upon the magnitude of pressure.

At a definite pressure the current density (in the range of 0.0016 amp./cm² ~ 0.0032 amp./cm²) and the material of electrode do not influence the current efficiency. It is expected that the current efficiency of this electrolysis is small in value and decreases with the increasing quantity of electricity because the solid sample under pressure can not diffuse itself in comparison with the electrolysis of solution.

Throughout this experiment the temperature change in compression or electrolysis is not observed practically and it is because of the large heat capacity of the high pressure apparatus and the thin thickness of samples.

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7) R. Kiyama and T. Yanagimoto, *This Journal*, **22**, 34 (1952)